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Research article

Conversion of coal mine drainage ochre to water treatment reagent: Production, characterisation and application for P and Zn removal

Devin Sapsford [a, *], Marco Santonastaso [a], Peter Thorn [b], Steven Kershaw [b]

[a] Cardiff School of Engineering, Cardiff University, Cardiff, UK
[b] Coal Authority, Mansfield, UK

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ABSTRACT

Coal mine drainage ochre is a ferruginous precipitate that forms from mine water in impacted watercourses and during treatment. With thousands of tonnes per annum of such ochre arising from mine water treatment in the UK alone, management of these wastes is a substantive issue. This paper demonstrates that the ochre from both active and passive treatment of coal mine drainage can be transformed into an effective water treatment reagent by simple acid dissolution and that the reagent can be used for the removal of dissolved phosphorous from municipal wastewater and zinc from non-coal mine waters. Ochre is readily soluble in H_2SO_4 and HCl. Ochre is more soluble in HCl with solubilities of up to 100 g/L in 20% (w/w) HCl and 68 g/L in 10% (w/w) H_2SO_4. For four of the eight tested ochres solubility decreased in higher concentrations of H_2SO_4. Ochre compositional data demonstrate that the coal mine ochres tested are relatively free from problematic levels of elements seen by other authors from acid mine drainage-derived ochre. Comparison to British Standards for use of iron-based coagulants in drinking water treatment was used as an indicator of the acceptability of use of the ochre-derived reagents in terms of potentially problematic elements. The ochre-derived reagents were found to meet the 'Grade 3' specification, except for arsenic. Thus, for application in municipal wastewater and mine water treatment additional processing may not be required. There was little observed compositional difference between solutions prepared using H_2SO_4 or HCl. Ochre-derived reagents showed applicability for the removal of P and Zn with removals of up to 99% and 97% respectively measured for final pH 7–8, likely due to sorption/coprecipitation. Furthermore, the results demonstrate that applying a Fe dose in the form of liquid reagent leads to a better Fe:P and Fe:Zn removal ratio compared to ochre-based sorption media tested in the literature.

1. Introduction

Ferruginous mine drainage from abandoned mines in the UK has a deleterious impact on the ecological and chemical status of receiving water bodies. Ochre is a term for the sludge, predominantly comprising hydrous ferric oxides, that precipitates from coal mine water and is accumulated by treatment systems during the treatment of mine drainage. The existing coal mine water treatment plants in the UK are all managed by the Coal Authority and treat predominantly circumneutral ferruginous mine water and lead to arisings of about 4500 tonnes of ochre (as dry) per year. Passive systems, which account for about 80% of the ochre production, create an ochre with very low solids content (<5%), and typically circa 30% Fe (dry weight). Active systems, produce ochre with a higher solids content but, due to the additives used, typically have an Fe content closer to 15% (dry weight). The ochre is stored within systems and/or dewatered and most is sent to landfill because there is currently no established beneficial reuse for ochre sludges in the UK. Landfill disposal costs for ochre are, at the time of writing, in the range £79/tonne to £129/tonne at a median 50% solids.

There have been numerous studies on reuse of mine drainage ochre, including the following examples: as a pigment in a range of industries (Hedin, 1998, 1999); as a component in brick manufacture and cement manufacture (Dudeney, 1997); for phosphate removal in sewage treatment works, in an unprocessed form (Wei et al., 2008) and in pelletized form (Heal et al., 2005; Littler et al., 2013; Sibrell et al., 2009); as an artificial soil additive (e.g.

* Corresponding author.
E-mail address: sapsforddj@cf.ac.uk (D. Sapsford).

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Evenson and Nairn, 2000); as a P-removing soil amendment (Fenton et al., 2012); as a feedstock for iron and steel manufacture; and as a substrate for adsorption of other metals in non-coal mine waters (Mayes et al., 2009). The only known commercial application to date is use as pigment (Hedin, 1999), although it has also been used in the UK within brick making albeit that this only offsets some of the disposal costs rather than generating commercial revenue. Whilst reuse options have been, and continue to be investigated a further problem is that apart from a few large capacity mine water treatment systems most sites are generally small producers of ochre waste and are geographically widespread. The top nineteen sites account for 80% of ochre arisings and, due to the volumes produced and the relative distances between them, deriving economic benefits without entailing excessive transport costs can be problematic. High value reuse applications are thus favourable and necessary.

This paper examines conversion of ochre waste to water treatment reagents. All major water utilities purchase iron-based reagents for water treatment; iron salts (principally ferric sulphate) are used as coagulants for colloid destabilisation or as a sweep floc in water treatment and as co-precipitants for the removal of dissolved forms of phosphorous during wastewater treatment. Therefore Fe-based reagents are extensively used in various water/wastewater treatment applications and thus present a promising high-value route for recycling ochre. Furthermore, the market demand for ferric reagents is large and easily sufficient to take all of the current UK ochre arisings after conversion to water treatment reagents.

Previous studies concerning use of ochre in water and wastewater applications have focussed on utilizing the ochre solid which has the ability to sorb phosphate and metal ions (Cornell and Schwertmann, 2003). Other literature has focussed on conversion of mine drainage and mine water treatment sludges for use as coagulants: Lopes et al. (2011) used mine water directly as a coagulant (and Fenton's reagent). Rao et al. (1992) tested acid mine drainage (AMD) as a direct coagulant and precipitated ochre from AMD dissolved in sulphuric acid to produce a coagulant (Fe 1.6 g/L) for settling clay slurries. The process of Menezes et al. (2009, 2010) involved precipitation of Fe from AMD followed by dissolution in sulphuric acid to produce a poly-alumino-iron sulphate coagulant which was proven successful for removal of suspended solids and colour.

Research has been undertaken on conversion of ferruginous and aluminiferous drinking water treatment sludges to coagulants and precipitants for P removal (e.g. Saunders et al., 1991; Vaezi, 2001; Abdo et al., 1993). The first process to achieve recycling of coagulant was patented in 1903 (Roberts and Roddy, 1960) and subsequently acid treatment followed by the membrane separation techniques has been investigated to recover and reuse coagulants in drinking water treatment (e.g. Sengupta and Shi, 1992; Stendah et al., 2005). Vaezi and Batebi (2001) used Fe-bearing water treatment sludge and sulphuric acid to produce ferric sulphate to use as coagulant in wastewaters from the textile industry. Other recovery methods have included alkaline treatment (Masschelein et al., 1985), liquid/liquid extraction (Dhage, 1985; Petruzzelli et al., 1998), reduction and acidification (Pigeon et al., 1978), a Donan membrane process (Prakash et al., 2004) and a composite membrane method (Li and Sengupta, 1995).

The aim of this research was to determine the potential for ochres from coal mine drainage treatment to be converted to Fe-based reagents for phosphorus (P) and zinc (Zn) removal. In the UK context the permissible levels of P in effluents from municipal wastewater treatment works into rivers continue to be reduced due to regulation driven by the European Water Framework Directive. The ochre-derived reagents were also applied to the removal of Zn from mine waters. Whilst progress with the discharges from abandoned coal mines is good, sustainable treatment methods for mine waters from metal mines containing very low amounts of iron but significant concentrations of metals such as zinc and copper are in their infancy with research underway currently to find a sustainable and effective treatment.

The specific aims of this research were to (i) determine compositions of parent ochres from a range of UK sites and solutions derived from them to identify whether there are detrimental levels of problematic elements present which might curtail their use (ii) determine the solubility of the ochre sludges in HCl and H_2SO_4 acids (iii) test ochre-derived reagent for application for the removal of P and Zn from real and synthetic solutions (iv) to compare removal efficacy of the ochre-derived reagents to laboratory reagent $Fe_2(SO_4)_3$ and $FeCl_3$ (these salts being the principal constituent of commercially available solutions for these applications).

2. Materials and methods

2.1. Ochre collection and characterisation

Ochre sludges were collected from a range of both active and passive mine water treatment sites in the UK, see Coal Authority (2014) for full listing of sites. Ochres were collected from passive mine water treatment plants in S.Wales: Taff Merthyr (near Trelewis); Lindsay (Capel Hendre), Glyncastle (Resolven); Morlais (near Llangennech). And from a site, Bates (Blyth) in England. Furthermore ochre from chemically dosed active mine water treatment systems were collected from Ynysarwed (Resolven, S.Wales – dosed with calic at 40% CaO); Dawdon (Seaham, England – dosed with hydrated lime slaked to 10% solution) and Blenkinsopp (Haltwhistle, England – dosed with caustic soda 47% solution). The Taff Merthyr ochre was used for the contaminant removal trials.

The samples were collected from the field, sealed in 5 L polypropylene containers and then stored at 5 °C. An aliquot of homogenised sample was dried for 24 h at 105 °C and then left to cool to room temperature in a silica gel desiccator. The dried ochre samples were microwave acid-digested using an Anton Paar Multiwave 3000 Microwave digestor system: approximately 0.1000 g (accurately known) of sample was dissolved in 6 mL of hydrochloric acid and nitric acid (1:1 HCl:HNO_3) and digested in the microwave with a temperature ramp of 10 °C min^{-1} up to 200 °C and held at that temperature for 30 min. The vessel content was diluted with deionized water and analysed for 28 elements by ICP-OES (Perkin Elmer Optima 2100D). Dried ochre samples were also used for a total carbon and sulphur measurement on a SC144DR Leco Furnace, and XRD analysis using a Phillips PW3830 x-ray generator with a Phillips Pw1710 controller.

2.2. Ochre solubility in HCl and H_2SO_4

The solubility of ochres in HCl and H_2SO_4 solutions of different acid strengths was measured by dosing increasing amounts of dried ochre (25–100 g/L) in the respective acid solutions. Acid solutions were prepared using analytical grade HCl (p.a., ≥32%) and H_2SO_4 (96% v/v) in 18 MΩ cm deionized (DI) water. The different mixtures were left shaking for 24 h in sealed Erlenmeyer flaks, then vacuum filtered through Whatman GF/A 1.6 μm glass microfiber filters. The solid residue left on the filter was dried for 24 h at 105 °C, left to cool to room temperature in a silica gel desiccator and finally weighed to calculate the amount of solute in each acid solution.

2.3. Preparation and composition of ochre-derived reagents

To prepare the ochre-derived reagents, an excess of dried Taff

Merthyr (TM) ochre was mixed in Erlenmeyer flasks with 1, 5, 10 and 20% (w/w) HCl and H_2SO_4 solutions. The mixtures were then sealed with laboratory film and shaken on an orbital shaker for 24 h at room temperature at 175 rpm. At the end of the shaking time, solutions were vacuum filtered through Whatman GF/A 1.6 μm glass microfiber filters and stored in sealed volumetric flasks. To serve as a comparison to testing with ochre-derived reagents, $FeCl_3$ and $Fe_2(SO_4)_3$ solutions were prepared using analytical grade Iron (III) sulphate hydrate and iron (III) chloride anhydrous dissolved in 18 MΩ cm DI water. Both the laboratory-derived reagents had a Fe concentration of 40 wt. %.

2.4. P and Zn removal experiments

P and Zn removal experiments were carried out using the TM ochre-derived reagents in 20% (w/w) acid. All measurements of pH were made using a Mettler Toledo Seven Multi S40 m along with an InLab Expert Pro ISM pH probe. All elemental analyses were carried out using a Perkin Elmer Optima 2100D. Two real effluents and two synthetic solutions were tested, as follows: (i) a treated wastewater collected from the final effluent of a treatment plant located in S.Wales (UK) with P content of 3.5 mg/L was used in the P removal trials. Whilst the speciation of P within the treated wastewater was not measured it is anticipated to be present predominantly as orthophosphate (ii) mine water from the former Frongoch mine (Mid-Wales, UK). This mine water was circumneutral with a Zn concentration of 16 mg/L (iii) A synthetic P solution was made up from analytical grade sodium phosphate monobasic monohydrate; 50 mg were added to 1 L of deionized water in order to create a 13 mg P/L solution. (iv) synthetic Zn solutions were prepared by using analytical grade zinc sulphate heptahydrate; 100 mg were dissolved in 1 L of deionized water in order to make a 27 mg/L Zn solution.

The Zn and P removal test were carried out using a Stuart flocculator SW6 at a stirring speed of 175 rpm for 1 h. For each test five repetitions were performed. Five borosilicate glass beakers were filled each with 1000 mL of solution, the pH was measured and samples withdrawn, filtered (0.45 μm) and acidified (0.1 ml of 10% w/w HNO_3) for ICP-OES analysis. After the initial sample was taken, specific amounts of the ochre-derived and laboratory reagents were added to the solutions to achieve circa 10 mgFe/L dose for Zn removal and between 59 and 291 mgFe/L for the P removal tests. In these experiments reagent doses for the real effluent were formulated as Fe doses (mg/L) calculated from the P-dosing equation in Metcalf et al. (2013) although it should be noted that the dose was higher than this because the measured P in the effluent was lower than had typically been measured on the day of wastewater sampling. pH was adjusted to achieve a final test pH of either 7 and 8 using NaOH (6 M) wherever required. After 1 h the pH was measured again; this final pH is reported in the results section. Aliquots were withdrawn from each of the 5 replicate tests, filtered, acidified and analysed by ICP-OES.

3. Results and discussion

3.1. Chemical characterisation of parent ochres and derived solutions

The 28 element data for the parent ochres are shown in Table 1. The Fe content (wt. %) varies for each of the sludges: Taff Merthyr, Ynysarwed and Glyncastle ochre all have a high Fe content, ranging between 46.18 and 48.68 wt. % whereas ochre sludges coming from Lindsay, Morlais, Bates and Blenkinsopp are characterized by slightly lower Fe contents, 33.15, 26.68, 31.19 and 35.67 wt. % respectively. Dried Dawdon ochre sludge was characterized by a very low Fe content (6.38 wt. %). XRD analysis performed on Taff Merthyr dried ochre sludge showed that the material consists mainly of goethite and a small proportion of SiO_2.

It is notable that the ochres contain relatively low concentrations of regulated and priority substances (often seen in AMD sludges) meaning that no additional processing to remove them is required. Arsenic (As) concentrations are equal or lower than 0.02 wt. % for all the ochres analysed. Cd, Cr, Ni, Pb and Sb were all found to be present in the ppm range, with Cd concentrations lower than the instrument detection limits. Sb also is present at very low concentrations and only in Taff Merthyr and Blenkinsopp ochres was it found to be present in concentrations higher than 5 ppm. The results for Cr, Ni and Pb show some variation but are all below 50 mg/kg with only Pb higher with values of 59.21 mg/kg and 78.10 mg/kg in Taff Merthyr and Ynysarwed ochre respectively. Selenium was below detection in all of the ochres analysed. Table 1 also shows the multi-elemental analysis of the reagents prepared by adding excess oven dried ochre to HCl and H_2SO_4 (20% w/w). The Fe contents for Taff Merthyr reagent in 20% HCl and H_2SO_4 were 4.8 wt.% and 0.92 wt.% respectively. Similar Fe contents were encountered in the other ochre-derived reagents. Reagents prepared using Lindsay, Morlais, Glyncastle, Bates and Blenkinsopp ochre exhibited Fe contents <2.4 wt. %. The main exception to these Fe values were the two reagents prepared using Dawdon dried ochre sludge; in this case Fe contents lower than 0.01 wt. % were measured for the derived reagents and the formation of a voluminous white precipitate (possibly $CaSO_4$) was observed during the preparation of the solutions. Note that the Dawdon sludge comes from the active treatment of a highly saline evaporite-influenced mine water which results in the relatively low Fe content of the ochre and high C (due to formation of $CaCO_3$). The other major elements identified by the ICP-OES analyses of the ochre-derived reagents were Si, S, Ca and in some cases Al. Interestingly, the resultant reagents are not rich in dissolved Al; possibly Al is present in the ochres as recalcitrant aluminosilicates bound with the iron precipitate. The presence of S comes from the oxidised and dissolved sulphur moiety of pyrite from the coal which generated the mine drainage. The Ca, Al, Si and Mg derive from the surrounding lithologies e.g limestones and mudstones.

3.2. Ochre solubility in H_2SO_4 and HCl

The solubility of the dried ochres determined in increasing strengths of HCl and H_2SO_4 solutions are presented in Fig. 1(a) and (b). The solubility data correspond to the Fe wt.% of the resultant 'reagent' solutions, shown in Fig. 1(c) and (d). As expected, ochre solubility generally increases with increasing acid strength. An important practical observation was that the presence of a residue in the bottom of the flask on addition of ochre did not mean that saturation had been reached, rather that there was an insoluble component of the ochre. It therefore took several experimental iterations to find the point at which the solution had lost its capacity to dissolve more ochre. Ochre solubility was higher in HCl with solubilities between 72 g/L (Ynysarwed) and 100 g/L (Bates) soluble in 20% (w/w) compared to highs of 63 g/L (Morlais) to 68 g/L (Ynysarwed) ochre at 10% H_2SO_4. The fact that lower ochre solubilities are seen at higher H_2SO_4 strengths is probably due to the formation of insoluble sulphate salts, which is seen strongly for experiments carried out with the Dawdon ochre where the weight change was positive due to formation of a salt product on reaction with the H_2SO_4. Given that the Dawdon ochre, is relatively low iron and is derived from the active (lime dosed) treatment of a highly saline mine water we suspect that a sulphate salt such as gypsum or natrojarosite formed.

The general differences in ochre solubilities in the two acids

Table 1
Multielemental analysis of ochres and ochre-derived reagents prepared in H_2SO_4 (20 w/w%) and HCl (20 w/w %). All the results are expressed in mg/kg unless otherwise stated.

Element content	Taff Merthyr			Ynysarwed			Lindsay			Morlais			Glyncastle			Bates			Dawdon			Blenkinsopp		
	Ochre	HCl	H_2SO_4	Ochre	HCl	H_2SO_4	Ochre	HCl	H_2SO_4	Ochre	HCl	H_2SO_4	Ochre	HCl	H_2SO_4	Ochre	HCl	H_2SO_4	Ochre	HCl	H_2SO_4	Ochre	HCl	H_2SO_4
Fe	48.68%	4.81%	0.92%	48.63%	4.25%	3.63%	33.15%	3.71%	0.65%	26.68%	2.91%	1.17%	46.18%	5.4%	2.27%	31.19%	3.99%	1.85%	6.38%	0.73%	38.59	35.67%	5.35%	2.11%
Na	232.1	5.50	2.25	296.5	22.50	50.30	975.3	29.10	2.10	944.7	25.20	nd	719.5	13.80	nd	1.38%	1911	885.0	1.26%	956.8	5.41	1534	29.40	17.20
Ca	1.130%	919.6	275.3	1.81%	2613	249.7	1.25%	1342	258.0	7072	687.9	288.5	2539	272.7	123.4	4.3%	3703	317.2	28.34%	3.13%	3.13%	5.45%	5671	328.5
Mg	1388	80.90	17.77	1084	1110	970.6	786.3	81.60	18.80	550.3	55.50	11.60	439.0	46.60	17.00	3774	412.3	218.8	3554	376.1	1.95	2665	256.6	120.5
K	980.8	7.60	1.54	323.1	12.30	13.60	402.2	20.60	8.30	210.2	11.60	5.10	167.3	5.40	2.20	515.9	56.60	28.80	665.8	47.70	0.30	1453	2.80	4.30
Mn	3413	314.8	60.83	1053	195.1	169.0	681.1	73.20	11.60	667.3	74.10	29.20	451.1	50.70	19.90	765.3	84.50	44.50	1335	155.3	0.83	1833	232.8	106.2
As	223.8	26.20	4.20	110.4	23.20	27.60	111.3	10.80	nd	63.25	11.20	9.10	186.9	18.60	12.00	35.88	5.20	5.20	43.69	4.80	0.09	65.33	7.30	6.60
Ba	422.9	30.90	0.29	457.4	2.80	2.10	278.9	15.20	0.10	103.6	9.40	0.30	21.44	1.20	0.30	59.23	0.60	0.30	20.41	0.60	nd	45.70	1.10	1.00
Cd	nd	nd	nd	nd	nd	1.60	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Cr	23.54	nd	0.29	10.10	nd	2.50	4.66	nd	nd	1.99	nd	nd	6.99	nd	nd	7.16	nd	0.40	nd	nd	nd	9.61	nd	0.60
Cu	0.02	nd	nd	4.35	2.60	0.20	9.78	nd	nd	10.96	nd	nd	29.36	nd	nd	26.57	nd	nd	28.86	nd	nd	22.32	nd	nd
Mo	nd	nd	nd	nd	nd	0.60	nd	nd	0.10	nd	nd	0.10	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Ni	17.55	nd	0.23	0.42	7.20	10.20	nd	nd	nd	nd	nd	nd	33.08	1.50	1.10	10.28	nd	0.10	nd	nd	nd	49.11	3.30	2.30
Pb	59.21	1.90	0.62	78.10	1.20	3.30	18.16	nd	0.20	11.95	nd	1.10	30.75	1.70	2.30	34.40	2.30	2.20	3.9	nd	nd	43.18	1.80	1.90
Sb	6.58	nd	0.04	1.04	0.20	2.60	nd	nd	nd	nd	0.30	nd	nd	nd	0.10	4.18	nd	nd	nd	nd	nd	7.00	0.40	0.40
Se	nd	nd	nd	nd	nd	nd	nd	nd	1.30	nd	nd	0.70	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Zn	117.4	43.20	2.43	139.9	11.10	10.40	146.7	8.40	2.60	44.82	nd	1.00	172.4	16.60	6.30	77.86	4.30	2.80	33.64	nd	0.01	118.0	7.90	5.60
Al	6607	14.40	4.08	700.5	386.5	323.6	842.6	3.60	nd	472.6	nd	nd	1399	122.3	37.70	529.8	nd	nd	685.8	1.10	0.18	2948	78.00	37.70
Li	5.50	nd	0.01	1.11	nd	1.50	nd	nd	nd	nd	nd	nd	nd	nd	nd	5.73	nd	0.40	13.20	0.20	0.01	2.15	nd	0.20
Be	1.31	nd	0.02	12.63	nd	2.40	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.26	nd	0.20	0.67	nd	nd	0.51	nd	0.20
Ti	41.07	nd	0.21	7.33	nd	3.10	32.12	nd	0.10	5.48	nd	nd	12.12	nd	0.10	13.65	nd	0.60	4.44	nd	0.01	93.06	nd	0.70
V	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sr	250.0	18.70	4.37	269.1	22.60	13.80	203.9	18.90	6.60	133.0	12.60	6.60	79.22	8.50	5.50	1786	144.5	34.90	4760	490.0	0.31	580.8	63.40	15.70
Tl	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.03	nd	nd	nd
Bi	6.47	nd	0.19	165.9	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Co	nd	nd	nd	nd	nd	2.80	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Ag	nd	nd	nd	nd	nd	0.50	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
S	1920	90.70	–	2459	251.6	–	875.2	73.80	–	1320	145.0	–	4316	492.8	–	4474	508.8	–	6693	375.9	–	2402	302.2	–
Si	9893	733.2	276.2	3.00%	76.70	47.80	1.96%	437.7	131.4	1.68%	711.0	258.7	2.45%	462.8	521.4	1.60%	nd	282.2	1.42%	nd	128.9	3.16%	353.3	433.4
C	1.93%	–	–	1.49%	–	–	1.06%	–	–	0.36%	–	–	0.36%	–	–	1.99%	–	–	9.81%	–	–	1.98%	–	–

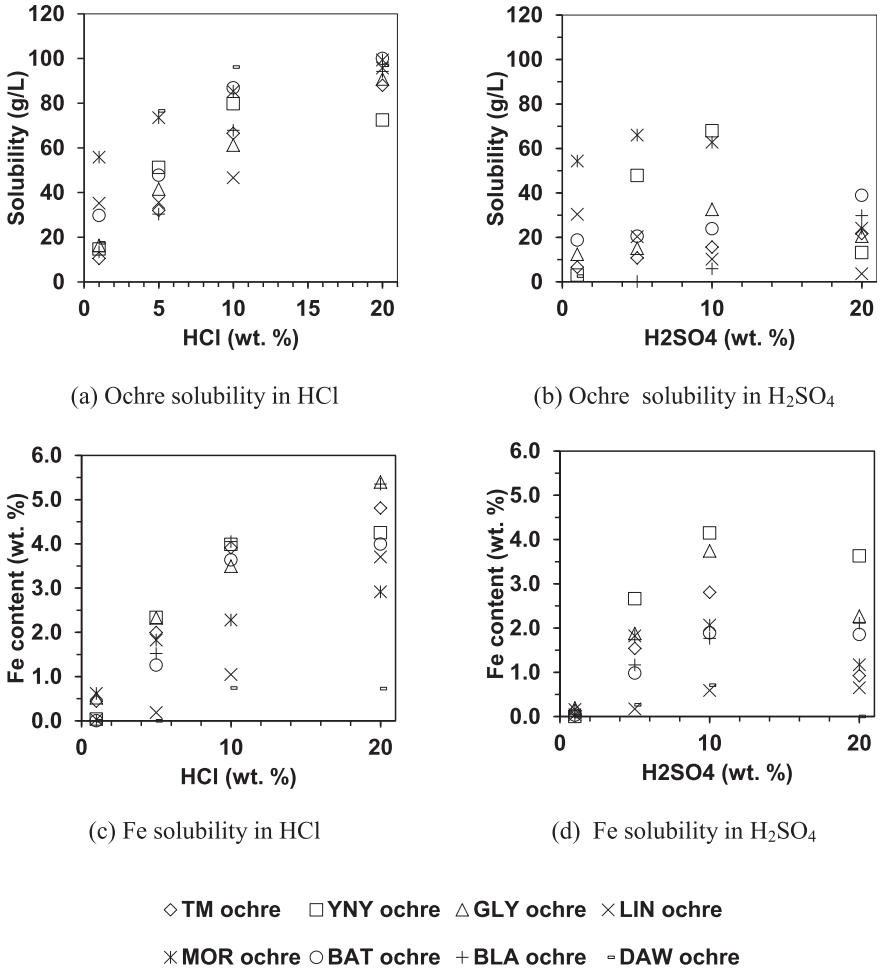


Fig. 1. Solubilities and corresponding Fe concentrations for ochres dissolved in hydrochloric acid and sulphuric acid of varying strength (w/w) data shown is maximum value from 5 experimental repeats (24 h contact time). TM = Taff Merthyr, YNY = Ynysarwed, GLY = Glyncastle, LIN = Lindsay, MOR = Morlais, BAT = Bates, BLA = Blenkinsopp, DAW = Dawdon.

might be expected from the stoichiometric considerations, which are that 2.63 kg H_2SO_4 per kg Fe and 1.96 kg HCl per kg Fe are required based on the dissolution of $Fe(OH)_3 3H_2O$ (Saunders and Roeder, 1991); this equates to solubilities (w/w) of 7.6% Fe for sulphuric acid solutions and 10% Fe for HCl solutions. Comparison of these maximum values (w/w) of 4.1% and 5.4% Fe with H_2SO_4 and HCl respectively in Fig. 1(c) and (d) demonstrate that these solubilities have not been reached in these experiments, but it should be noted that these are ideal solubilities for an idealised formula of iron compound.

3.3. Preparation of water treatment reagents: comparison of chemical composition of ochre-derived reagents to standards

Ochre from Taff Merthyr (TM) was used for further characterisation and testing. Whilst there are no compositional standards available to conform to for ferric reagents applied in wastewater treatment, the elemental compositions of TM ochre-derived reagents are here compared to standards for ferric coagulants used in drinking water application. It is noteworthy that these are rigorous standards in terms of permissible contaminants because of their use in drinking water treatment for human consumption. Table 2 gives the compositions of the TM ochre-derived reagents compared with the limits set by the BS EN 888:2004 and BS EN 890:2012 standards that define the permissible materials/concentrations for use for the treatment of water for human consumption when using $FeCl_3$ and $Fe_2(SO_4)_3$ based coagulants. In these standards the elemental contents are expressed in proportion to the Fe (III) content, as a percentage for Mn and mg/kg of the Fe (III) content for other elements. Three grades of coagulant purities are reported. It can be seen from Tables 2 and 3 that the TM ochre-derived reagents do not conform to Grade 1 (although Cd, Cr and Ni are within specification for all acid strengths), nor to Grade 2, but meet the Grade 3 criteria except for As. This means that further processing would be required for the use of this ochre-derived reagent in the treatment of water for human consumption. However, because it almost meets standards for use in water treatment applications the authors contend that it should not be considered problematic for wastewater applications, subject to plant specific consents.

3.4. Removal of phosphate by ochre-derived reagents

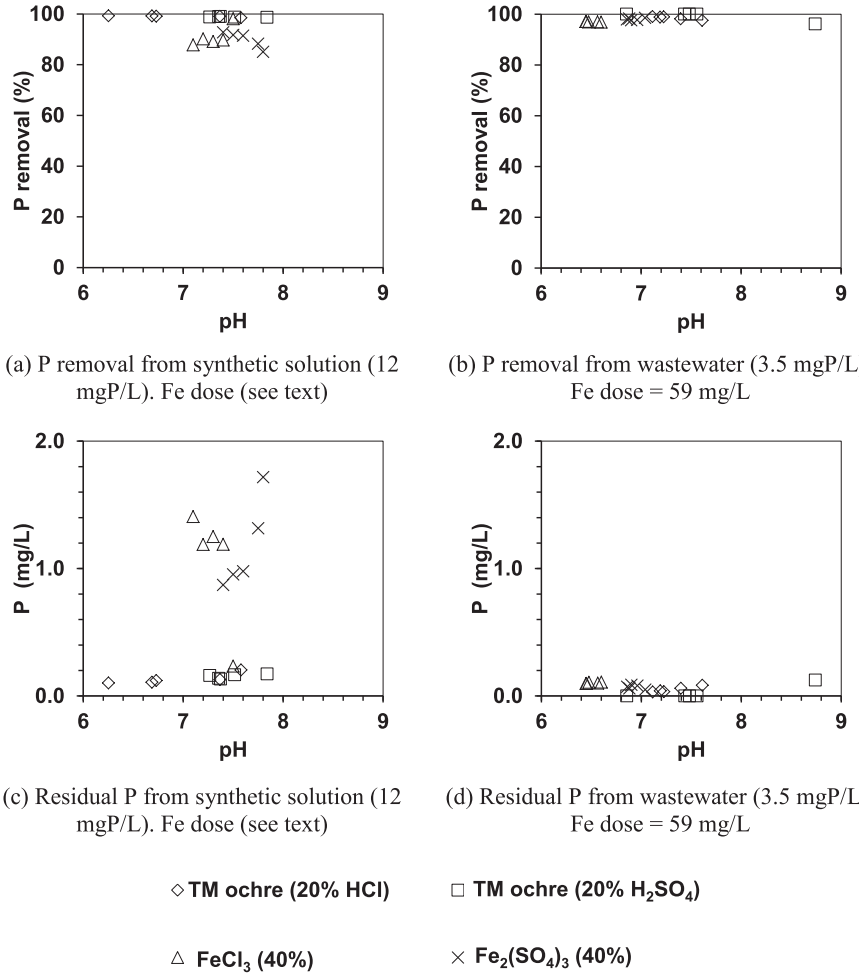
Fig. 2(a) and (c) illustrates the results obtained from the P removal trials conducted the synthetic $NaHPO_4$ solution (P = 13 mg/L) with a dose of 291 mgFe/L (TM-HCl) and 276 mgFe/L (TM-H_2SO_4) for ochre-derived reagents and 96 mgFe/L and 83 mgFe/L for laboratory reagents ($Fe_2(SO_4)_3$ and $FeCl_3$ respectively). Given the sensitivity of adsorption and co-precipitation phenomena to pH, the removal data is plotted versus final pH. Both the ochre-derived reagents and the laboratory reagent removed P from the solution to low levels; ochre-derived reagents in HCl (20 w/w %)

Table 2
Metals concentrations expressed as a proportion (either % or mg/kg) of the Fe(III) content in the Taff Merthyr ochre-derived reagents in HCl of different % strength compared with the limits set by the BS EN 888:2004 standard for Grades 1–3.

	Mn (%)	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Se (mg/kg)
BS Grade 1 Limits	0.5	20	1	50	60	35	10	10
BS Grade 2 Limits	1	20	25	350	350	100	20	20
BS Grade 3 Limits	2	50	50	500	500	400	60	60
TM-HCl (1%)	0.5	222.2	<0.9	35.7	10.5	152.6	29.6	<29.6
TM-HCl (5%)	0.5	88.1	<0.5	34.0	19.6	116.1	14.5	<16.9
TM-HCl (10%)	0.7	122.3	<0.3	31.9	29.0	97.7	6.1	<8.9
TM-HCl (20%)	0.7	496.1	0.6	45.9	38.2	94.2	11.9	<8.6

Table 3
Metals concentrations expressed as a proportion (either % or mg/kg) of the Fe(III) content in the Taff Merthyr ochre-derived reagents in H_2SO_4 of different % strength compared with the limits set by the BS EN 890:2012 standard for Grades 1–3.

	Mn (%)	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Se (mg/kg)
BS Grade 1 Limits	0.5	1	1	100	300	10	10	1
BS Grade 2 Limits	1	20	25	350	350	100	20	20
BS Grade 3 Limits	2	50	50	500	500	400	60	60
TM-H_2SO_4 (1%)	0.5	125.0	<0.7	35.5	35.3	64.5	16.8	<24.3
TM- H_2SO_4 (5%)	0.5	157.0	<0.5	33.4	20.2	75.2	21.2	<17.1
TM- H_2SO_4 (10%)	0.6	261.5	<0.4	31.9	22.6	60.1	8.7	<12.2
TM- H_2SO_4 (20%)	0.7	454.9	<0.3	31.3	24.5	67.5	4.6	<10.8



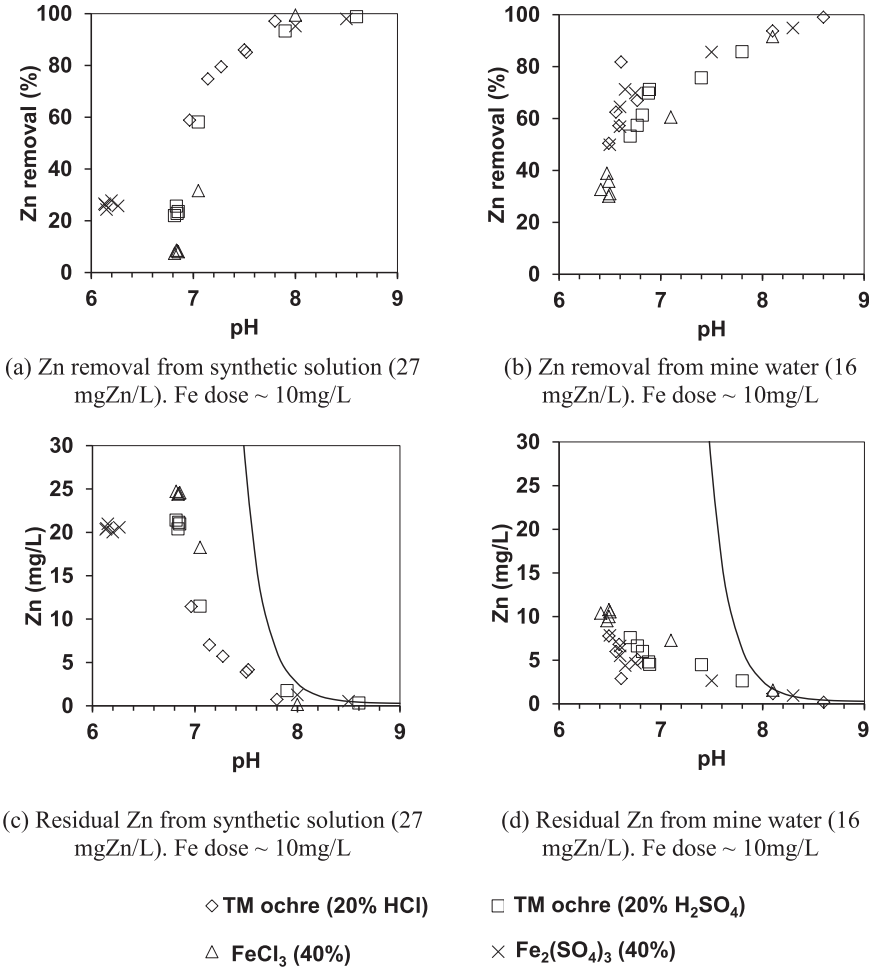
(a) P removal from synthetic solution (12 mgP/L). Fe dose (see text)

(b) P removal from wastewater (3.5 mgP/L). Fe dose = 59 mg/L

(c) Residual P from synthetic solution (12 mgP/L). Fe dose (see text)

(d) Residual P from wastewater (3.5 mgP/L). Fe dose = 59 mg/L

Fig. 2. Results of P removal experiments dosing synthetic sodium phosphate solution and a real wastewater with Taff Merthyr (TM) ochre-derived reagents and comparison with laboratory reagents $FeCl_3$ and $Fe_2(SO_4)_3$.



(a) Zn removal from synthetic solution (27 mgZn/L). Fe dose ~ 10mg/L

(b) Zn removal from mine water (16 mgZn/L). Fe dose ~ 10mg/L

(c) Residual Zn from synthetic solution (27 mgZn/L). Fe dose ~ 10mg/L

(d) Residual Zn from mine water (16 mgZn/L). Fe dose ~ 10mg/L

Fig. 3. Results of zinc removal experiments dosing synthetic zinc sulphate solution and mine water with ~10mgFe/L Taff Merthyr (TM) ochre-derived reagents and comparison with laboratory reagents $FeCl_3$ and $Fe_2(SO_4)_3$. Curve on each graph shows the solubility of $Zn(OH)_2$.

and ochre-derived reagents in H_2SO_4 (20 w/w %) gave P-removals of on average 99% after 1 h. TM ochre-derived reagents outperformed the laboratory reagents (albeit at higher dose) regardless of final pH, as can be seen from the residual P concentrations of (mean ± stdv) of 0.18 ± 0.02 mg/L for TM-H_2SO_4 and 0.13 ± 0.04 mg/L for TM-HCl (Fig. 2(a)) compared to 1.17 ± 0.31 mg/L and 1.05 ± 0.42 mg/L for laboratory reagents ($Fe_2(SO_4)_3$ and $FeCl_3$ respectively).

For the wastewater, tertiary treatment effluent doses of 59 mgFe/L were applied in all cases, which allows comparison of performance between ochre-derived and laboratory reagents. P-removal performances of both the ochre-derived reagents and laboratory reagent were very high with removal percentages between 97 and 100 % for all the reagent types (Fig. 2(b)). The initial P concentrations were lower on the sampling day than previously measured, leading to an overdose according to the Metcalf et al. (2013) formula. The removal of P in all cases was excellent, with the TM ochre-derived reagents leaving residual P concentrations below detection limit of the ICP-OES (0.01 mg P/L) when using TM-H_2SO_4 and of (mean ± stdv) of 0.05 ± 0.02 mg P/L when using TM-HCl.

This compares with residuals of 0.07 ± 0.01 mg P/L and 0.10 ± 0.00 mg P/L for laboratory reagents $Fe_2(SO_4)_3$ and $FeCl_3$ respectively (Fig. 2(d)). These results are all well below typical UK

Table 4
Ratio of P removed to Fe dose (mass basis) for ochre-derived reagent P-removal trials compared with ratios derived from P removal trials carried out in other studies. Based on Fe content of ochres as given in those references. Mean removal and residual data are reported for this study.

Study	Reagent/Adsorbent	Water type	Ratio of P removed to Fe dose	Residual P (mg/L)
This study[a]	TM-HCl reagent	Wastewater	1: 18	0.05
	TM-H_2SO_4 reagent	Wastewater	1: 18	<0.01
	TM-HCl reagent	Synthetic	1: 21	0.1
	TM-H_2SO_4 reagent	Synthetic	1: 21	0.2
Dobbie et al. (2009)	Polkemmet Ochre (max from field trial data (2b))	Wastewater	1: 27	3.8[b]
Sibrell and Tucker (2012)	Blue Valley AMD sludge	Wastewater	1:44	1
Wei et al. (2008)	Coal acid mine drainage ochre from active treatment site	Wastewater	1:26	0.21

[a] Mean removal and residual phosphorus.
[b] From Fig. 3(a) of cited paper.

discharge consents of 1 mg P/L. For these trials, differences in final pH between different tests did not affect the final P removals of the trials suggesting that the pH is well above the sorption edge for P onto the precipitates and/or that co-precipitation and/or precipitation of iron phosphate are important.

3.5. Removal of zinc by ochre-derived reagent

Fig. 3(a) and (c) display the results from the Zn removal experiments carried out on synthetic Zn-bearing water after dosing with 10 mgFe/L from laboratory reagents and 9.2 mgFe/L (TM-H_2SO_4) and 11.6 mgFe/L (TM-HCl) from ochre-derived reagents. An important consideration in evaluating these removal percentages is the final test pH which was slightly different in each case (Fig. 3(c) and (d)). Aqueous Zn concentrations are controlled by both mineral solubility and sorption to iron precipitates which are both pH dependent phenomena, consequently the end pH will be important for determining Zn removals by the reagents. The $Zn(OH)_2$ solubility curve derived using PHREEQCi (Parkhurst and Appelo, 2013) is shown in Fig. 3(c) and (d). It can be seen that at pH > 8 the removal is probably due at least in part to precipitation of $Zn(OH)_2$, thus this data is not considered further. However, at pH < 8 it can be seen that the Zn concentrations are reduced substantially in the presence of the precipitating Fe, probably by a combination of sorption and co-precipitation.

The data in Fig. 3 show that with the ochre-derived reagents Zn removal was typically better than that of the laboratory derived reagents for removing Zn from the synthetic Zn sulphate solution (27 mgZn/L) at pH < 8. The TM-H_2SO_4 reagent removed a maximum of 93% Zn with a 1.75 mgZn/L residual (final pH 7.90), the TM-HCl reagent removed a maximum of 97% Zn with a 0.74 mgZn/L residual (final pH 7.80). The laboratory $Fe_2(SO_4)_3$ reagent removed a maximum of 28% Zn with a 20.01 mgZn/L residual (final pH 6.20). The laboratory $FeCl_3$ reagent removed a maximum of 32% Zn with a 18.26 mgZn/L residual (final pH 7.05).

The data in Fig. 3 show that with the ochre-derived reagents Zn removal was also typically better than that of the laboratory derived reagents for removal of Zn from the circumneutral Frongoch mine water (mgZn/L) at pH < 8. The TM-H_2SO_4 reagent removed a maximum of 86% Zn with a 2.63 mgZn/L residual (final pH 7.80), the TM-HCl reagent removed a maximum of 82% Zn with a 2.90 mgZn/L residual (final pH 6.61). The laboratory $Fe_2(SO_4)_3$ reagent removed a maximum of 85% Zn with a 2.64 mgZn/L residual (final pH 7.50). The laboratory $FeCl_3$ reagent removed a maximum of 60% Zn with a 7.27 mgZn/L residual (final pH 7.10).

3.6. Reagent consumption

The data presented in Tables 4 and 5 provide the ratio of the mass of either P or Zn to mass of Fe removed in the experiments using the ochre-derived reagents, these are compared to values derived by P and Zn removal trials by other authors on to ochre or pelletised ochre. The data are presented in this way to normalise the contaminant (P or Zn) removal to the Fe content which enables comparison of the reagent consumption when applying Fe in liquid form (this study) or solid form (other studies).

The addition of ochre-derived reagents for P (Table 4) results in slightly better P:Fe removal ratio than using ochre in its unprocessed solid form, and with slightly lower residual P concentrations. This may because when Fe from the ochre-derived reagents precipitates out, the precipitate has a higher reactive surface area for sorption and coprecipitation of P. The mass removal ratios for the laboratory-derived ochre were even higher, with mean removal ratios of Fe:P of 1:8.9 and 1:8.0 albeit leaving higher residual concentrations of 1.05 and 1.17 mg P/L for $FeCl_3$ and $Fe_2(SO_4)_3$ respectively.

Processing the ochre to a liquid form for treatment confers a slight advantage in terms of w/w P removal over using the ochre in its 'as received' form, but is disadvantageous with respect to the cost for processing to the dissolved form and the acidity of the ochre-derived reagent, which may require pH correction where wastewaters have insufficient buffering capacity. These disadvantages need to be set against the advantages which are: (i) the production of a potentially valuable product for the wastewater industry where there is established practice of using liquid ferric sulphate, and (ii) the relative ease of transportation, pumping and metering of liquids compared to solids.

The removal ratio of Zn to Fe using ochre-derived reagents was significantly different compared to the same ratios calculated from results published in related research (Table 5). Zn:Fe ratio using the ochre-derived reagents range from 1:1 to 1:0.5. Previous works by Cui et al. (2013) and Mayes et al. (2009) reported Zn to Fe ratios much higher than those presented from this work, with the lowest ratio reported by Mayes et al. (2009) of 1:43 (leaving an average of 0.9 mgZn/L in solution) using pelletized ochre in a field trial. The significantly lower ratio found in this study indicates coprecipitation of Zn with Fe and may mean that Fe dosing using ochre-derived reagents is viable for Zn load removal and that processing to liquid form has beneficial effect on reagent consumption for removal of Zn as compared using ochre solids.

4. Conclusions

- Ochre is a common waste arising from mine water treatment. This study has demonstrated a simple means of processing ochre from mine water treatment (both active and passive) to produce a potentially commercial reagent for P and Zn control in wastewaters and mine waters.
- Ochre is readily soluble in H_2SO_4 and HCl. Ochre is more soluble in HCl with solubilities of up to 100 g/L in 20% (w/w) HCl and

Table 5
Ratio of Zn removed to Fe dose (mass basis) for ochre-derived reagent Zn-removal trials compared with ratios derived from Zn removal trials carried out in other studies, based on Fe content of ochres as given in those references. Mean removal and residual data are reported for this study.

Study	Reagent/Adsorbent	Water type	Ratio of Zn removed to Fe dose	Residual Zn (mg/L)
This study	TM-HCl reagent	Mine water	1: 1.0	See Fig. 3
	TM-H_2SO_4 reagent	Mine water	1: 0.8	See Fig. 3
	TM-HCl reagent	Synthetic	1: 0.5	See Fig. 3
	TM-H_2SO_4 reagent	Synthetic	1: 0.7	See Fig. 3
Cui et al. (2013)	Coal mine drainage sludge	Synthetic (pH 6–8)	1: 110[a]	<0.8 mg/L
Mayes et al. (2009)	Pelletized hydrous ferric oxide	Mine water (pH 8.7)	1: 43	0.9 mg/L[b]

[a] Calculated from the reported 70 percent goethite content of cmds25.
[b] Mean effluent data from Table 1 of cited reference.

68 g/L in 10% (w/w) H_2SO_4, corresponding to Fe concentrations of 5.4% and 4.1% Fe (w/w). For some ochres solubility actually decreased in higher concentrations of H_2SO_4 with solubility limited by the formation of a precipitate.

- ➢ The ochres examined were relatively free from problematic elements, compositions of the ochre-derived reagents met the BS EN 888:2004/890:2012 'Grade 3' specification for coagulants used in drinking water, except for As. There was little difference in composition between solutions prepared using H_2SO_4 or HCl.
- ➢ Ochre-derived reagents were effective for the removal of P and Zn from synthetic solutions and real wastewaters at pH 6.0–8.6 with P removal to below detection (0.01 mg P/L) for final effluent from a wastewater treatment works and up to 86% Zn removed from mine water (final pH 7.80)
- ➢ Ochre-derived reagent were found to result in a higher removal of Zn for a given Fe dose compared to data from the literature on using ochre in solid form, indicating that processing of ochre to dissolved iron is beneficial in terms of lower iron consumption.

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